

X-Ray Line Broadness of Metals and Alloys and Its Relation to High Temperature Stability

By J. E. WILSON and L. THOMASSEN



**REPRINTED from the TRANSACTIONS of the
American Society for Metals, Cleveland, Ohio**



X-RAY LINE BROADNESS OF METALS AND ALLOYS AND ITS RELATION TO HIGH TEMPERATURE STABILITY

BY J. E. WILSON AND L. THOMASSEN

Abstract

Recovery of X-ray line sharpness in cold-worked metals and alloys is studied as a function of time and temperature of annealing. Line sharpening is caused by diffusion of displaced atoms to normal lattice positions; in the case of nickel at low annealing temperatures, the process involves a long induction period. A quantitative time-temperature relationship for line sharpening is determined for nickel, copper and the alpha brasses. A mechanism of recovery, based on correlations with hardness, electrical conductivity and other data, is described.

Line sharpening temperatures may be used to predict immunity from "season cracking" in brasses.

Creep data on brasses, copper-nickel alloys and a series of pearlitic manganese and manganese-molybdenum steels are correlated with line broadness data. In a continuous series of solid solutions, the alloy of maximum line-sharpening temperature has the optimum creep characteristics. The poor creep strength of 60-40 brass above 500 degrees Fahr. is due to inferior temperature stability of the beta phase. A secondary maximum in creep strength at 900 degrees Fahr. in one of the manganese-molybdenum steels is paralleled by a maximum in a precipitation hardening effect which is disclosed by X-ray and hardness measurements.

INDUSTRIAL requirements for materials of good high temperature properties have increased enormously in the past decade. The outstanding qualifications for such service are high limiting creep stresses and resistance to corrosion and oxidation under operating conditions. The behavior of metals and alloys at high temper-

This paper is based on a dissertation submitted by J. E. Wilson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

Of the authors, J. E. Wilson is metallurgist for the Kelvinator Corp., Detroit, and L. Thomassen is assistant professor of Chemical Engineering, University of Michigan, Ann Arbor, Mich. Manuscript received August 9, 1934.

atures has therefore become very important to the metallurgist, and probably will be for years to come.

The most direct way of investigating the high temperature properties of an alloy is to subject it to tests that simulate operating conditions as nearly as possible or convenient. Tests of this sort are necessarily time consuming and limited in applicability to the particular alloy in question.

Creep is essentially plastic deformation which occurs at such a temperature that the strain-hardening is partially offset by the isothermal softening or recovery. The equilibrium creep rate at a given temperature and stress is dependent on the difference between rates of strain-hardening and recovery and on the inherent cohesion properties of the particular metal or alloy under observation. Examination of this problem from the point of view of the general behavior of cold-worked metals and alloys on annealing might accordingly be expected to yield valuable correlations. Among the properties which might be studied are hardness, electrical conductivity, magnetic induction, and X-ray diffraction effects. The last named property has served most extensively as a tool in the present investigation.

In 1925 van Arkel (1)* reported that the X-ray diffraction lines produced by the powder method (Hull-Debye-Scherrer method) were made broadened and diffuse for a number of cold-worked metals, and that this effect disappeared on annealing. Similar observations were reported by Davey (2) on tungsten powders.

This effect has since been investigated somewhat more thoroughly, but the reported experiments are not all in agreement. It is generally accepted that the broadening is due to internal strains rather than extremely fine grain size. (3, 4, 5) There is, however, a wide spread of opinion as to the role this type of lattice distortion plays in the other observed effects of plastic deformation such as hardening and decrease of electrical conductivity. One group of investigators (4, 5) has advanced the hypothesis that the lattice distortion revealed as X-ray line broadening is responsible for the hardening of metals on cold-working based on an alleged parallelism between the increase of hardness and the line broadness with the degree of deformation.

Others (3) believe that the broadening is a result of a special kind of lattice distortion and is more or less independent of strain-

*The figures appearing in parentheses refer to the appended bibliography.

hardening. This belief is based on the existence of strain-hardening in certain metals, such as aluminum, which do not show appreciable broadening of X-ray lines after deformation at room temperature.

Published data and theory concerning the recovery of line sharpness on annealing are not in good agreement. Dehlinger (3, 6) believes that the sharpening temperature coincides with the recrystallization temperature, while Sekito (7) thinks that line broadness decreases gradually with increased annealing temperature. Burgers and van Arkel (8) maintain that for any annealing temperature below the recrystallization temperature the broadness diminishes quickly to a constant end value, and that a fixed unsharpness remains for each annealing temperature. These conclusions, however, were based only on experiments with tungsten wires.

MATERIALS INVESTIGATED

This investigation falls in two parts. In the first part, pure metals were investigated; in the second, alloys, on which creep test data were available, were studied. In order to eliminate anomalous behavior due to impurities, an effort was made to obtain as pure samples as possible for the first part of the investigation. For the second part, we were also fortunate in obtaining samples of brass and of an unusual series of pearlitic manganese steels from the Department of Engineering Research of this University, through Dr. C. L. Clark, who also furnished us with samples of Adnic and Monel metal. All of these samples have been investigated by Clark and White so that very complete creep data were available.

EXPERIMENTAL TECHNIQUE

In order to eliminate the degree of deformation as a variable, all the pure metals were worked as severely as possible, that is, to incipient failure, while in the alloys, the degree of deformation was kept as constant as possible throughout each series. Except for certain special experiments, all of the cold-working was done by means of a belt hammer at room temperature, care being taken to dip the small specimens in water between the blows of the hammer to prevent any appreciable heating.

The strips of work-hardened material were then cut into specimens one-half inch square, numbered, ground and polished. After the polishing operation, the samples were given the desired annealing

treatment in an electric furnace controlled by a potentiometer controller. To further decrease the temperature variations, specimens were inserted in a cast iron annealing block. Temperatures were read with a portable potentiometer which was calibrated against a precision potentiometer. The chromel-alumel couple used had been calibrated against the melting point of pure zinc. Its readings were

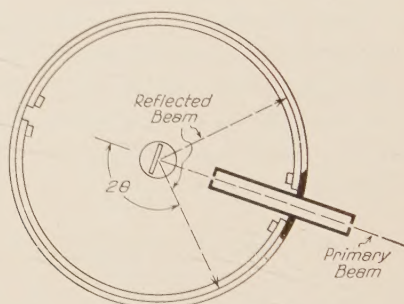


Fig. 1—Sketch of Debye Camera.

also compared to those of a calibrated mercury thermometer and a proper correction curve worked out.

The time of annealing in this report is the designated period after the specimen has come to the desired temperature. In all cases the furnace was at temperature when the specimens were inserted. The time required for specimens to reach the desired temperature was found to lie between two and four minutes. After annealing, the samples were severely deep-etched to relieve any surface strains not representative of the body of the metal.

X-ray diagrams were then taken of the samples by placing the prepared surface parallel to the axis of a cylindrical camera so that the axis was in the plane of the surface. The diameter of the cameras used was 205 millimeters and the beam of X-rays striking the surface at a 90-degree angle was diffracted from the surface of the sample to the cylindrical film. This "back reflection" method has the advantage that the lines of largest angle of diffraction will be present, thus giving the maximum resolution of the $K\alpha$ doublet, so that the breadth determinations can be made on a single line. A sketch of the camera is shown in Fig. 1.

In Fig. 2 is shown typical diagrams of a cold-worked and of an annealed specimen of brass. The radiation used was the Fe-K radiation generated in a demountable X-ray tube of the Siegbahn-Hadding

type. The exposure times were between 30-40 milliamperes-hours at 20 KV peak.

Broadness of the lines was determined by use of the large model Moll microphotometer. The results are expressed in terms of the breadth of the $K\alpha_1$ line at one-half its maximum blackening. Photom-

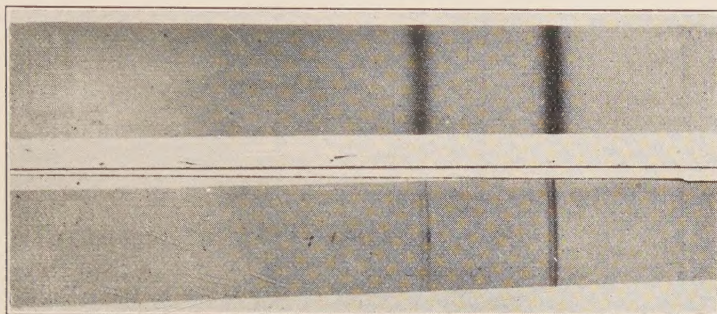


Fig. 2—"Back-Reflection" X-Ray Diagrams; Upper Diagram Shows (222) and (113) K Lines of Cold-Worked 70-30 Brass, While Lower One Shows Same Lines in Specimen Annealed at 280 Degrees Cent.

eter magnification is 7 times except where otherwise noted. Fig. 3 shows typical photometer traces. A typical series of measurements are given in Table I.

RESULTS

Pure Metals

Aluminum—Van Arkel (1) and Dehlinger (3) in their work on broadening of X-ray lines on cold working of metals report that the lines of several of the soft metals including lead, tin, zinc and aluminum were not broadened by cold work. On the basis of these results, Dehlinger has proposed a different mechanism of cold working for aluminum than for other metals.

Considering the low melting points of these metals, it may be probable that there is a connection between these and the temperature of working of the metal which presumably is room temperature. It was, therefore, decided to determine if aluminum could be made to fall in line with the other metals by working it at a lower temperature. A cold drawn piece of this metal was therefore annealed for three hours at 250 degrees Cent. (480 degrees Fahr.). Specimens were then compressed in a universal testing machine, some at room temperature and some at -76 degrees Cent. (-105 degrees Fahr.). In

the latter operation the samples were immersed in acetone, cooled by dry ice, for fifteen minutes before the compression began. The compressed specimen was transferred to an X-ray camera and the

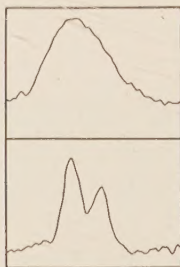


Fig. 3—Moll Microphotometer Traces for Cold-Worked and Annealed Brasses.

exposure completed within two hours. The measurements of the photometric records are shown in Table I.

Table I
Measurements of Photometric Records

Treatment	$\frac{1}{2}$ Value Line Broadness (28X) Millimeters
Annealed	22.2
Worked at 25 degrees Cent. (77 degrees Fahr.)	23.6
Worked at -76 degrees Cent. (-105 degrees Fahr.)	35.8

As will be seen, the sample worked at the lower temperature has an appreciable increase in line broadness.

Copper—Cylindrical specimens of annealed copper were compressed at the desired temperatures under a load of 3000 kilograms, cooled quickly in air, etched, and X-ray pictures prepared. The results shown in Table II indicate that copper, as well as aluminum, may be worked at such a temperature that no line broadening will result.

Table II
Measurements of Photometric Records of Copper Specimens

Deformation Temperature	$\frac{1}{2}$ Value Breadth* (113) $K\alpha_1$
25 degrees Cent. (77 degrees Fahr.)	16.4 millimeters
150 degrees Cent. (300 degrees Fahr.)	18.0 millimeters
260 degrees Cent. (500 degrees Fahr.)	21.4 millimeters
400 degrees Cent. (750 degrees Fahr.)	19.2 millimeters
510 degrees Cent. (950 degrees Fahr.)	10.7 millimeters

*Microphotometer magnification is $\times 28$.

In addition to these experiments, the material was cold-forged in the standard manner to a reduction of thickness of 90 per cent, then annealed for 1-hour periods at selected temperatures. Broadness of the (113) line is plotted against annealing temperature in Fig. 4. The curve indicates the rapid recovery within a narrow temperature range; in this case it is less than 40 degrees Cent. (105

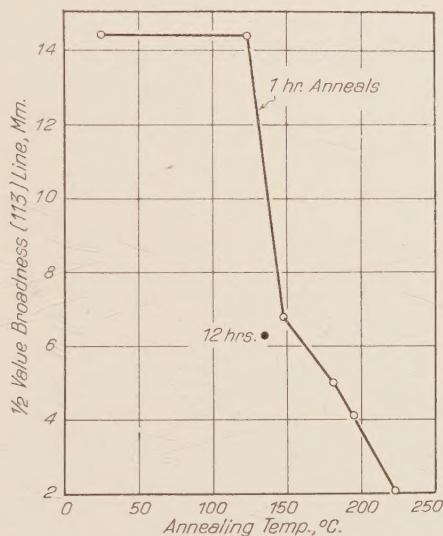


Fig. 4—Recovery of High Purity Copper from Line Broadness.

degrees Fahr.). At annealing temperatures above 150 degrees Cent., (300 degrees Fahr.) individual sharp spots appear in the continuous powder lines, indicating that gross recrystallization is beginning.

Nickel—The material was cold-forged to a reduction of thickness of 75 per cent after annealing one hour at 700 degrees Cent. (1290 degrees Fahr.), then tested according to the standard procedure. The results of the line broadness measurements on the (113) lines are reproduced in Figs. 5, 6, and 7. The annealing treatments were planned so as to study the effect on line broadness of the two variables present, namely, time and temperature, keeping first the one, then the other, constant, and finally investigating the course of line sharpening for various annealing periods.

The amount of sharpening produced by various heating times at 512 degrees Cent. (955 degrees Fahr.) is shown in Fig. 5. There

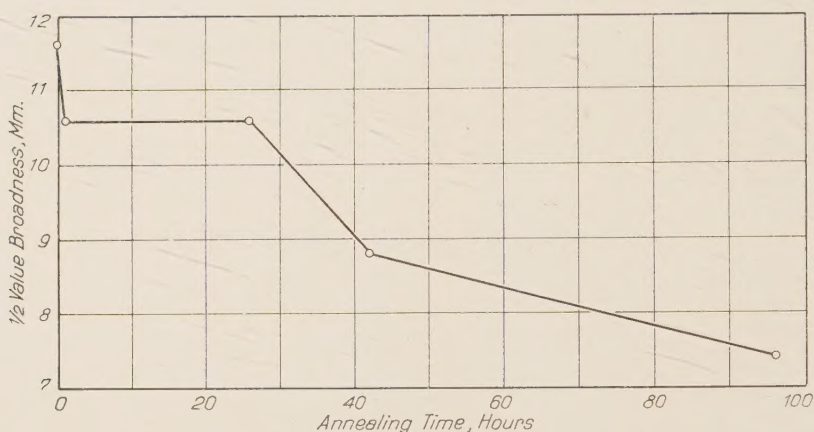


Fig. 5—Effect of Time at 512 Degrees Cent. on Width of (113) Line of Nickel.

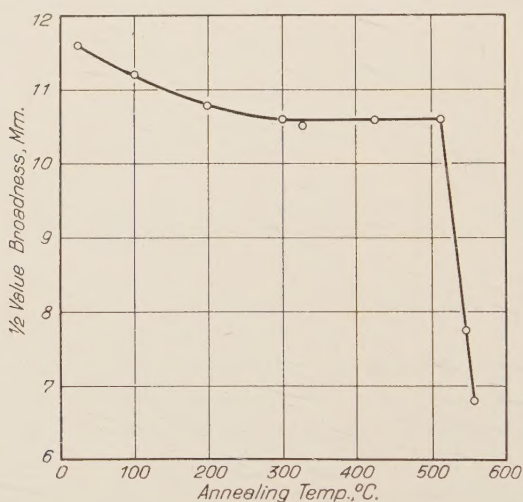


Fig. 6—Effect of One Hour Anneals at Various Temperatures on Broadness of (113) Line of Cold-Worked Nickel.

is almost no change from 1 hour to 26 hours, and relatively rapid sharpening takes place between 26 and 42 hours. Then a slow sharpening occurs on further heating.

The effect of 1-hour anneals at various temperatures is shown in Fig. 6. The line broadness shows a slight but definite drop in the interval 25 to 300 degrees Cent. (77-570 degrees Fahr.), and then

remains constant to 512 degrees Cent. (955 degrees Fahr.). In the temperature interval 512 to 564 degrees Cent. (955-1050 degrees Fahr.) the drop is sharp, changing from 10.6 at the former to 6.8 at the latter temperature. At 564 degrees Cent. (1050 degrees Fahr.) distinct resolution of the doublet was observed so the anneals were stopped.

The course of line sharpening for various annealing periods is shown in Fig. 7. The specimens were annealed for various lengths

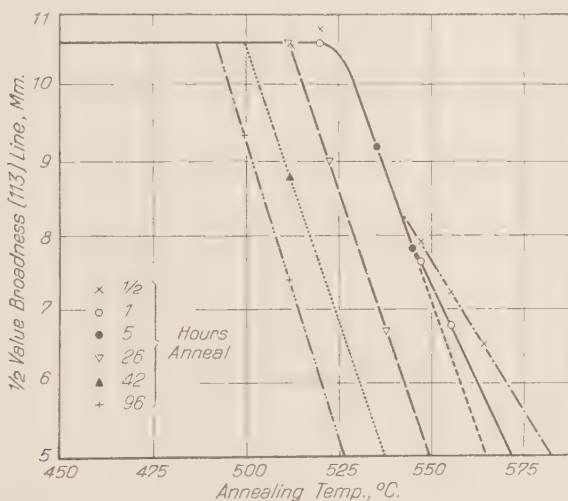


Fig. 7—Recovery of Line-Sharpness on Annealing Cold-Worked Grade A Nickel.

of time at chosen temperatures and the results seem to show that the recovery of line sharpness takes place over a broader temperature range in short-time than in long-time anneals. More particularly, Fig. 7 shows that there is little difference in slope of recovery curves for anneals of 5 hours or longer and that the slope becomes progressively flatter for the 1-hour and 30-minute series.

In order to reduce these data to a common basis, the individual curves have been extrapolated to half-value widths of 5.0. This value was chosen because it corresponds to the lowest broadness value attained with this metal without introducing complications due to recrystallization. The temperatures at this half-value have been plotted against the logarithms of the corresponding annealing time in Fig. 8. The straight line shown was considered the best fit for the data.

Iron—Specimens of cold-worked Armco iron were annealed for 1 hour and X-ray diagrams prepared. Broadness measurements were made on the (220) and (211) lines, with results as reproduced in Fig. 9. It is noteworthy that although the amount of broadening is greater for the higher order lines, in confirmation of experimental

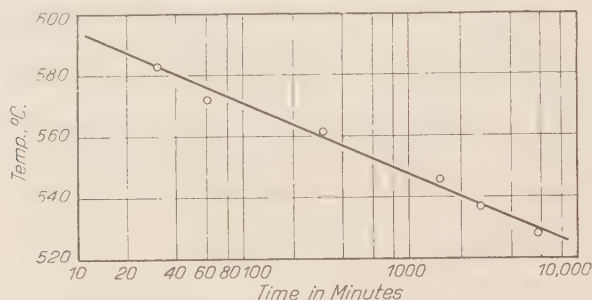


Fig. 8—Relation Between Time and Temperature of Annealing Grade A Nickel to Attain Constant Line-Sharpness of 5.0.

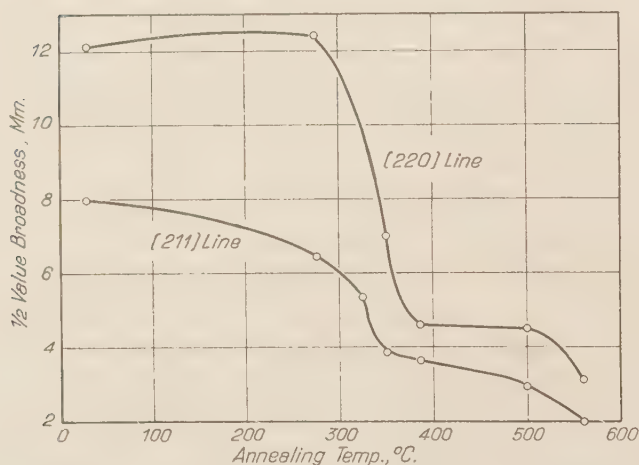


Fig. 9—Recovery of Armco Iron from Line Broadness. One Hour Anneals.

results of Wood (9) and of Caglioti and Sachs (10), the temperature of inflection points of the recovery curves are independent of the order of line. The dormant period in line sharpening from 400-500 degrees Cent. (750-930 degrees Fahr.) is followed by a secondary sharpening which corresponds to the formation of individual sharp spots on the lines which correspond to gross recrystallization grains, rather than the general recovery from line broadness.

Summary of Experimental Results for Pure Metals

(1) The temperature of working affects the amounts of broadening attainable as shown by copper and aluminum.

(2) In the case of iron, the amount of broadening is greater for higher order lines but the course of line sharpening is essentially the same; i.e., the inflection points of the recovery curves occur at the same temperature for both sets of lines.

(3) The temperature range of line sharpening becomes progressively greater for annealing times less than 5 hours in the case of nickel.

(4) The time for a constant recovery effect as shown by constant line broadness is a logarithmic function of the annealing temperature of nickel.

COPPER-ZINC ALLOYS

Three brasses of wide commercial application were tested—namely, the 85-15, 70-30 and 60-40 alloys. The compositions are given in Table III.

Table III
Chemical Compositions of Selected Copper-Zinc Alloys

Designation	Copper Per Cent	Zinc Per Cent
R-85	85.00	14.92
B	69.48	30.44
E-1*	60.21	39.72

*Contains 0.16 per cent tin.

The annealed alloys were cold-forged until they cracked. This occurred at a reduction of between 85 and 90 per cent. The samples were annealed in the usual way. Broadness measurements were obtained on the (222) line. Hardness measurements were made on these specimens and plotted along with some of the line sharpening curves.

85-15 Brass—From Fig. 10 it will be seen that the major portion of the sharpening has been accomplished at about 265 degrees Cent. (510 degrees Fahr.) for the 1-hour anneals, at which temperature the hardness has just begun to drop. The drop in broadness for this annealing time and for ten minutes, twelve hours and 107 hours is shown in Fig. 11, with a more extended temperature axis. The tendency here is, as in the case of pure nickel, that there is a larger temperature range of sharpening for short-time than for

long-time anneals. Sharp spots were not noticed on the lines from specimens which had been annealed for 1 hour at temperatures less than 300 degrees Cent. (570 degrees Fahr.), indicating that gross recrystallization involving grain growth does not occur at much lower temperatures. The flat foot portion of the recovery curve corresponds to the inception of softening and gross recrystallization.

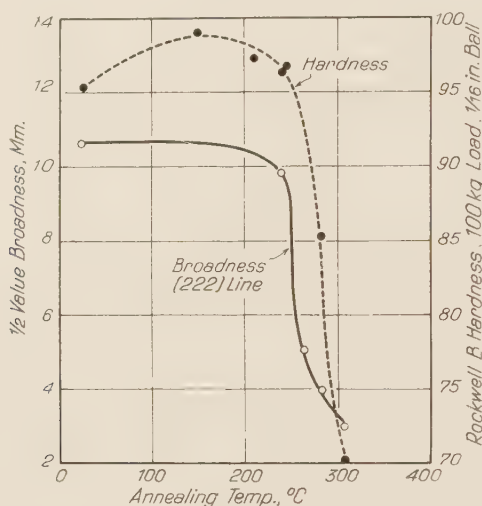


Fig. 10—Recovery of Cold-Worked 85-15 Brass, Annealed for 1 Hour.

70-30 Brass—Fig. 12 indicates sharpening of lines and recovery from work hardening in the 70-30 composition. The characteristics of these curves are the minor increase in hardness of brass in intermediate temperatures, and the extreme rapid drop in line broadness apparent in the temperature range 245-255 degrees Cent. (475-490 degrees Fahr.). In this range, about 90 per cent of the sharpness is restored, while the recovery from work hardness amounts to only 20 per cent.

The curves for the recovery of line sharpness with varying annealing times are reproduced in Fig. 13. These are the results of a limited number of experiments, but they seem to prove that rate of sharpening with respect to temperature is constant for annealing times of one hour or more.

60-40 Brass—This alloy is composed of two solid solution phases of different lattice structure. In order to study the recovery of this alloy from the effects of cold work, both the α and the β phases were

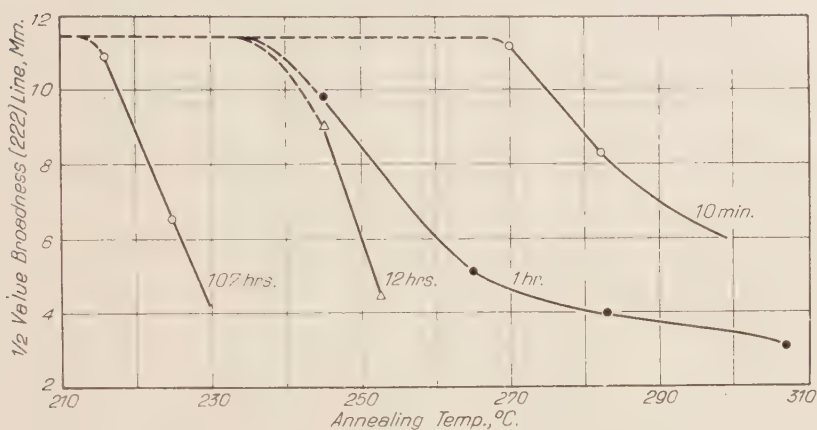


Fig. 11—Recovery of Line Sharpness on Annealing Cold-Worked 85-15 Brass.

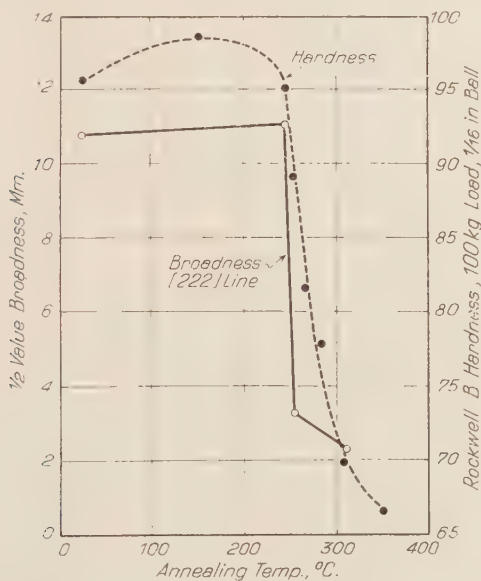


Fig. 12—Recovery of Cold-Worked 70-30 Brass. Annealed for One Hour.

investigated. It is easily seen that the X-ray method furnishes an ideally simple method of attaining this goal. Fig. 14 shows the recovery of line sharpness for the (222) and the (220) lines from the α and the β phases, respectively, together with the Rockwell hardness for specimens annealed 1 hour at the indicated temperatures. These

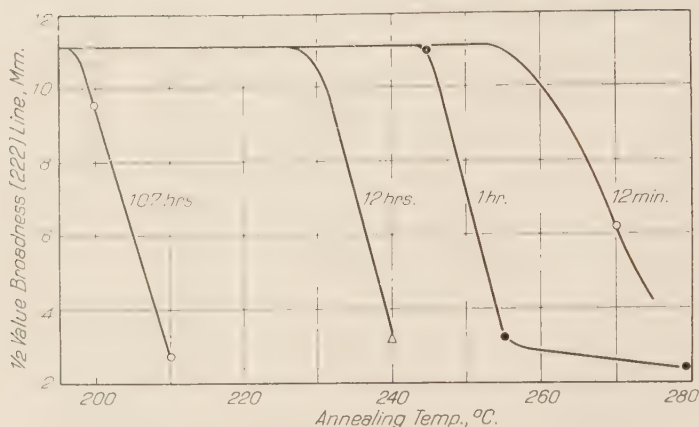


Fig. 13—Recovery of Cold-Worked 70-30 Brass From Line Broadness.

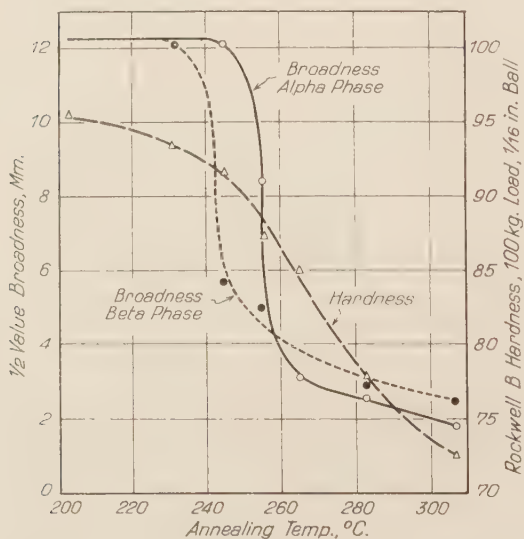


Fig. 14—Recovery of Cold-Worked 60-40 Brass. One Hour Anneals.

curves clearly show that the recovery from the effects of cold work has its inception in the β phase at a lower temperature than in the α phase. The hardness recovery is apparently an average effect of the two phases as would be expected from the nature of the test.

ADNIC AND MONEL METAL

These alloys were chosen as representative copper-nickel alloys of commercial importance. The chemical analysis of the samples used are shown in Table IV.

Table IV
Composition of Adnic and Monel Metal

	Copper	Nickel	Per Cent	Iron	Tin
Adnic	70	29		...	1
Monel	29.7	67.7		1.77	(Mn) 1.28

The presence of iron, manganese and tin prevent their being true copper-nickel alloys but it was felt that the results obtained would be of more general interest than those found on synthetic alloys of high purity.

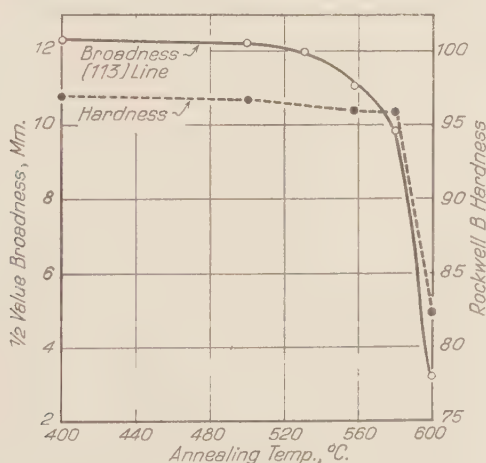


Fig. 15—Recovery of Monel Metal. One Hour Anneals.

The experiments with these alloys were limited to 1-hour anneals, and as Figs. 15 and 16 show, the recovery takes place over a rather broad temperature range in both alloys. The region of rapid sharpening is between 575 and 600 degrees Cent. (1065-1110 degrees Fahr.) for the Monel. In the case of Adnic, the recovery is apparently a 2-stage process with drops occurring between 400 and 500 degrees Cent. (750-930 degrees Fahr.) and again between 560 and 580 degrees Cent. (1040-1075 degrees Fahr.).

PEARLITIC STEELS

The alloyed steels which were made the subject of this investigation include a series of carbon-manganese steels ranging from 1.62 to 2.67 per cent manganese, a series of carbon-manganese steels varying between 1.25 to 3 per cent manganese with constant additions of

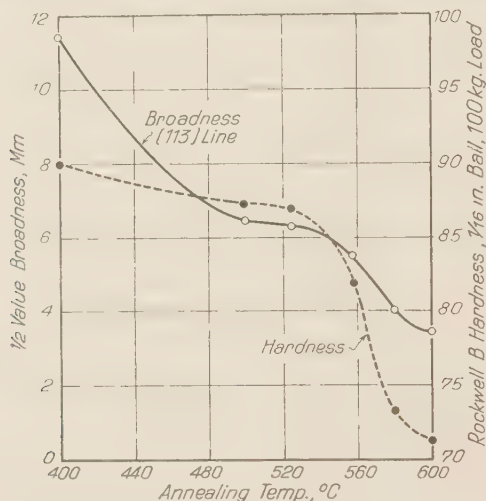


Fig. 16—Recovery of Cold-Worked Adnic. One Hour Anneals.

about 0.25 per cent molybdenum, and a carbon-manganese-molybdenum steel modified by the addition of vanadium. The chemical analyses are given in Table V. The amount of carbon present is about 0.16 per cent and nearly constant for all steels.

Table V
Chemical Compositions of Selected Alloyed Steels

Designation	C	Mn	Mo	V	Si	P	S
	Per Cent						
MM-5	0.14	1.62			0.15	0.019	0.017
MM-6	0.16	2.10			0.22	0.020	0.024
MM-7	0.18	2.67			0.10	0.018	0.028
MM-10	0.15	1.10	0.20		0.36	0.028	0.018
MM-8	0.15	1.25	0.25		0.19	0.028	0.018
MM-1	0.17	1.40	0.22		0.33	0.018	0.020
MM-9	0.15	1.75	0.25		0.15	0.017	0.024
MM-2	0.15	2.06	0.21		0.19	0.019	0.019
MM-3	0.17	2.52	0.26		0.15	0.020	0.030
MM-4	0.16	2.99	0.24		0.23	0.024	0.017
QV	0.18	2.00	0.32	0.20	0.23	0.016	0.025

The preparation of the samples was as follows: Bars of 1-inch diameter were annealed above their critical temperatures and furnace-

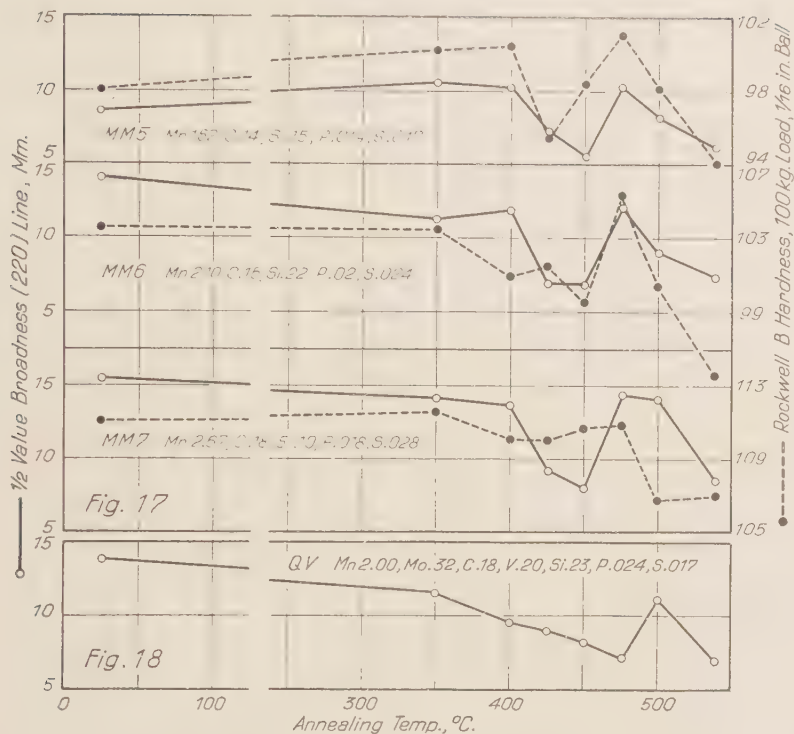


Fig. 17—Hardness and Sharpness of (220) Lines of Cold-Worked Manganese Steels After 2-Hour Anneals at Indicated Temperatures.

Fig. 18—Sharpness of (220) Lines of Cold-Worked QV Steel After 2-Hour Anneals at Indicated Temperatures.

cooled, and then reduced in a shaper to flats of $\frac{3}{8}$ -inch thickness. The flats were cold-forged to $\frac{1}{4}$ inch thickness, thus giving a plastic deformation of 33 per cent on the original thickness. The specimens were then treated as before, except that the temperature was controlled to only plus or minus 6 degrees Cent. After the specimens had been heated 2 hours at the desired temperature, the current was shut off, and the samples allowed to cool in the furnace. To get comparable results, samples of each composition were assembled in sets, and annealed simultaneously at the designated temperature.

In Figs. 17 to 19 are graphically summarized the X-ray and hardness data obtained on these series of steels. The curves show a general parallelism between broadness and hardness measurements, but the recovery is more complex, due apparently to a hardening of the precipitation type. The significance of the individual curves will be discussed later.

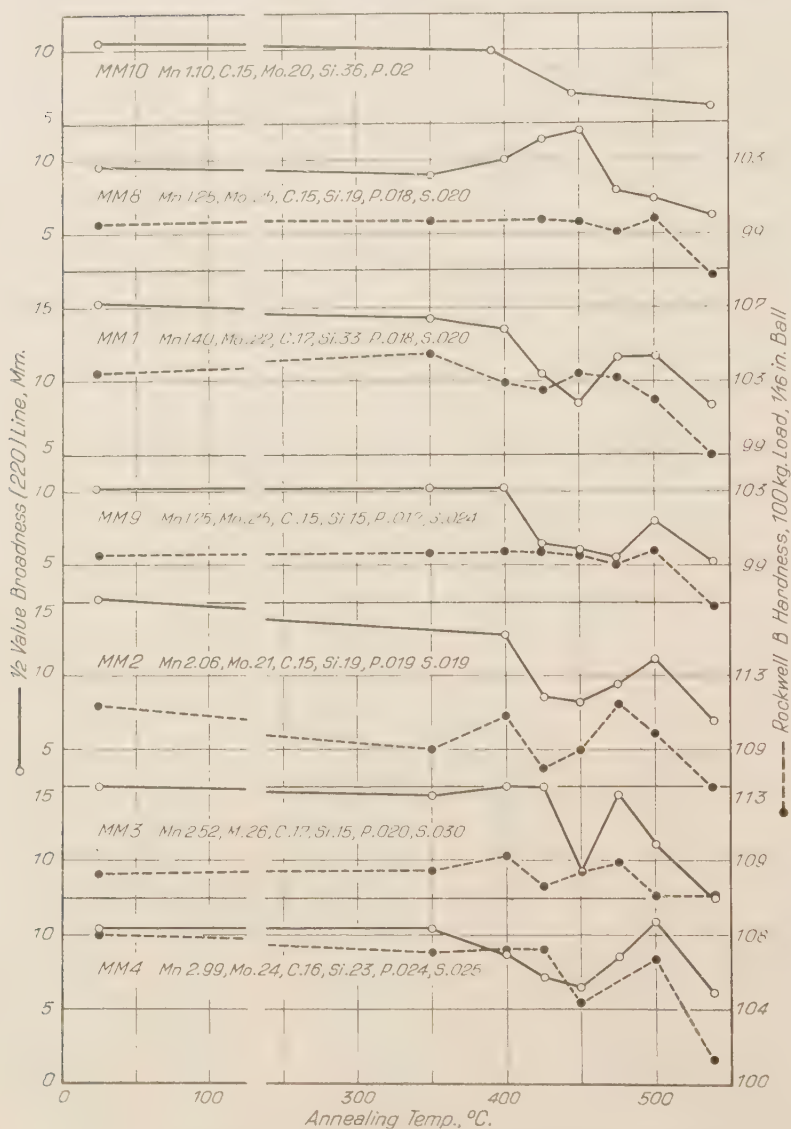


Fig. 19—Sharpening of (220) Lines of Cold-Worked Manganese-Molybdenum Steels on Annealing Two Hours at Indicated Temperatures.

INTERPRETATION OF RESULTS

These results, when considered in their relation to other known phenomena of the recovery of metals and alloys from the effects of

cold-work, lead to a conception of the mechanism of plastic deformation and recovery which is in many ways similar to previously advanced hypotheses but which requires modification of certain accepted concepts for agreement with the assembled data.

Data from the literature on such effects of plastic deformation as have been noted by electrical, magnetic and hardness measurements are included in the following discussion. The mechanism of plastic deformation and recovery obtained by these correlations is applied particularly to the questions of season cracking in brass and to the creep properties of metals at elevated temperatures. It is shown that the X-ray data give good agreement with accelerated season cracking tests and the creep data on the alloys studied in this investigation.

PLASTIC DEFORMATION OF ALUMINUM AND COPPER

It was shown in the experimental part that aluminum can be worked at such a temperature that line broadening results, and that, on the other hand, copper can be worked at such a temperature that the lines remain sharp although the converse is true at room temperature in each case. Dehlinger (3) advanced the hypothesis that metals like aluminum, zinc, tin and lead do not exhibit line broadening on cold-working (presumably at room temperature) because the lattice is bent or crumpled sharply in some parts with long intervals of undistorted lattice between. This type of crumpling reduces the probability of line broadening, according to the Laue conception of the space lattice. Dehlinger believes this type of deformation is inherent to such metals; however, he did not discuss the effect of deformation temperature. Expressed as a ratio of deformation temperature to melting point in absolute Centigrade units, room temperature or "cold" working is performed at 0.32 for aluminum, and at 0.22 for copper. By reducing this ratio to 0.24, broadening was produced in aluminum. This indicates that a change in the nature of lattice crumplings is in some way connected with the ratio of deformation to melting temperature of the material.

There are, however, differences in the plastic deformation of aluminum and copper which may be ascribed only to differences in atomic structure associated with their positions in periodic classification of the elements. Thus, aluminum retains hardness due to working at room temperature for an indefinite period; whereas, the data of Sauerwald and Globig (11) indicate that copper worked at tem-

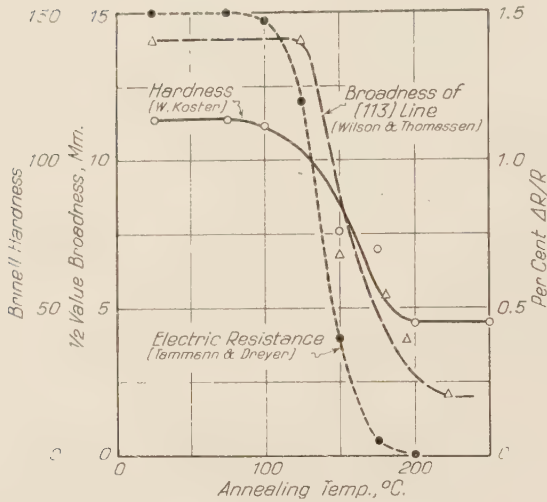


Fig. 20—Recovery of Cold-Worked Copper.

peratures which do not result in line broadening will lose its work hardness in a relatively short time. This is also brought out by the fact that the temperature at which no broadening occurs in pure copper is 0.55 when expressed as a ratio to the melting point compared to 0.32 for aluminum at room temperature.

Recovery of Pure Metals from Effects of Cold Work

Such differences as were pointed out between aluminum and copper also become evident on examination of data on the cold-working and annealing of copper, iron, and nickel. The ways in which differences in atomic structure affect the deformation and recovery characteristics are clarified by a study of the line broadness and hardness data in conjunction with results available in the literature on electrical conductivity and magnetic induction as well as certain other effects.

Recovery of Copper—It was suggested in discussing the plastic deformation experiments that differences in behavior of copper and aluminum were due to differences in atomic structure. Some of the salient features of the recovery of copper are reproduced in Fig. 20. The hardness data are taken from the work of Koster (12) for a degree of cold work corresponding to that used in the X-ray experiments. He found, however, that the inflection point of hardness

recovery curve varied between 90 and 390 degrees Cent. (95-735 degrees Fahr.) as the degree of reduction decreased from 93 to 3 per cent, thus showing a large dependence of recovery temperature on the degree of deformation.

The curves show that the recovery of line sharpness, hardness and electrical conductivity all occur at almost identical temperatures. This coincidence has been used by certain investigators as evidence that the type of atom distortion responsible for strain hardening is also the cause of electrical resistance changes. If this is true, the effects should also be parallel in their increase during plastic deformation. However, according to Tammann and Dreyer (13), the hardness increases rapidly with lower degrees of deformation, the curve becoming almost asymptotic to the degree of deformation axis between 90 and 98 per cent reduction, while the increase of electrical resistance is very slow up to 60 per cent reduction, it then increases rapidly as reductions approach 100 per cent.

W. A. Wood (4), and Caglioti and Sachs (10) both found that the line broadness of copper increases in a manner which is somewhat similar to the hardness, in that it increases more rapidly with lower degrees of deformation. However, Caglioti and Sachs were unable to show complete parallelism for these effects and their calculations indicate that energy must be stored in the lattice in some form other than that evident as line broadening.

The change in electrical conductivity of copper on cold-working cannot in the face of these data be ascribed to the same type of lattice distortion which causes either the hardening or the line broadness. Consideration of the above facts has suggested the following explanation of the mechanism by which the various phenomena of cold-working and recovery of copper occur.

As deformation progresses, in addition to slip, there occurs a displacement of atoms within the extent of each atom block comprising a slip lamella, probably according to a more or less definite period as pictured by Dehlinger (3). This atomic displacement is partially elastic in nature, particularly with small amounts of strain. However, the forces at grain and slip lamella boundaries are so great that actual deformation of outer shell electrons occurs, with the result that cohesion bonds are changed to a molecular type for such boundary atoms. This concept is in a way similar to the hypothesis of Dean and Gregg (14); the atoms so affected are only boundary atoms and due to their small number affect the electrical conductivity but

little; whereas, the hardness or resistance to further slip is greatly increased. The idea of boundary atom deformation has been advanced previously by Dehlinger, who emphasizes the factor of geometric roughening of slip planes, and accordingly is in agreement with the slip interference theory of Jeffries and Archer (15), in that both ascribe hardening to slip interference caused by roughening of the boundary planes.

Experimental verification of this boundary atom deformation is found in the work of Hengstenberg and Mark (16), who observed that the intensity of reflection for high order lines was markedly reduced in duralumin by the age hardening process, although the breadths of lines were unchanged.

As deformation progresses, the binding of so-called "free" electrons with consequent formation of molecular type cohesion bonds occurs in the interior of atom blocks. This causes decreased electrical conductivity. As an additional factor, the formation of extreme preferred orientations becomes effective at very great degrees of deformation. This factor is probably contributory to decreased electrical conductivity in copper by diminution of electron free path.

On annealing, the bound electrons are freed by input of thermal energy and the unstable molecular bindings change to normal lattice forces and the displaced atoms which cause line broadening return by a diffusion process to normal positions. The sequence of changes which occur on annealing may thus be summarized:

1. Thermal vibration of individual atoms is inhibited by the molecular type bondings. These bonds are decomposed by heat allowing the less stable molecules of the interior of slip lamella to dissociate.

2. This dissociation frees valence electrons and the electrical conductivity is recovered.

3. Thermal vibration of individual atoms occurs in the interior of slip lamella, allowing displaced atoms to diffuse back to normal positions. This results in line sharpening. The relief of internal strains in the interior of atom blocks results in a certain stage of the process in an actual increase in forces on the boundary atoms which causes a condition of abnormal stress at these points, as evidenced by often observed increase in hardness after low temperature anneals.

4. The diffusion of atoms of the body of the lattice block to normal position eliminates the abnormal force components on the atoms of slip planes; the molecular bonds and atom displacements are then eliminated by the further influence of heat and the softening process occurs.

5. Gross recrystallization consists of a diffusion process by

which two or more lattice blocks of the order of magnitude of 10^6 centimeter which have returned to normal condition according to the described processes are joined by a slight change in orientation.

The energy distribution in the cold-worked lattice is Maxwellian in nature, according to evidence of Zickrick and Dean (17) and by van Liempt (18), so the above described processes overlap to an extent which depends on the nature of the metal. In copper the energy

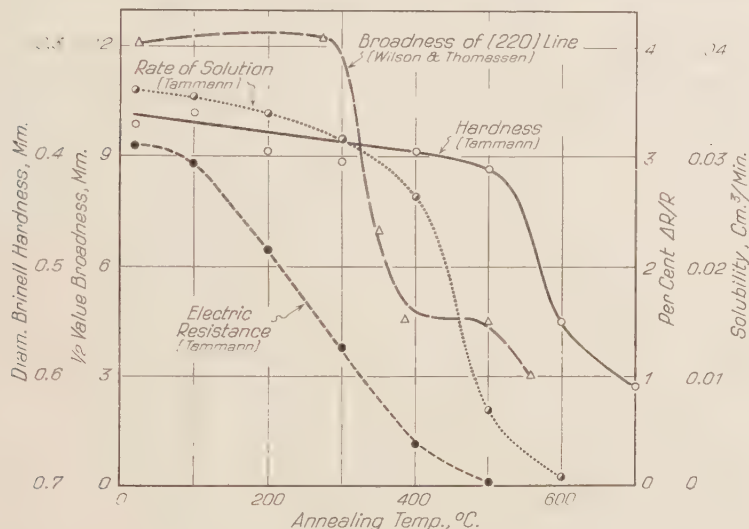


Fig. 21—Recovery of Cold-Worked Iron.

requirements of the decomposition of molecular bonds are apparently only slightly different than those for atomic diffusion and the temperatures for the observed phenomena are accordingly almost identical.

Recovery of Iron—Fig. 21 illustrates the main features of the recovery of iron from the effects of cold work. The data on electrical and magnetic recovery and on rate of solution in reagents are due to Tammann and Moritz (19). These curves show a wide temperature difference for the occurrence of maximum rates of recovery of various properties as shown by the inflection points of the curves. In iron the steps in the recovery process, which are hard to separate in copper, are distinct and easily traced. The inflection point of recovery of electrical conductivity occurs at approximately 250 degrees Cent. (480 degrees Fahr.), and according to the findings of Tammann and Moritz, this point is not affected by the degree of

deformation. The next inflection point, or point of maximum rate of change, occurs in the recovery of line sharpness, which is found to lie at approximately 345 degrees Cent. (655 degrees Fahr.), followed at 430 degrees Cent. (805 degrees Fahr.) by the inflection point of the decrease in rate of solution of iron, and by the corresponding point for hardness drop at 550 degrees Cent. (1020 degrees Fahr.), which coincides with a secondary drop in line broadness between 500 and 600 degrees Cent. (930-1110 degrees Fahr.).

These stages of the annealing process follow very clearly the mechanism outlined in the discussion of the recovery of copper. The iron atoms initially vibrate as molecular units under the influence of heat. This causes the input of sufficient energy for a dissociation process to occur, which results in the observed increase in electrical conductivity. The concept of decreased free path of electrons caused by disordered lattice arrangement is insufficient to explain the decrease in electrical conductivity of iron since if this were the case, the recovery of electrical conductivity should coincide with the elimination of line broadness. The latter effect is induced by the diffusion of individual atoms to normal lattice positions, after vibration of individual atoms is made possible by dissociation of molecular bondings.

The next phenomena in order of temperature is the decrease in rate of solution of iron, which occurs in a temperature interval during which the recovery of line sharpness is dormant. This recovery phenomenon is due to the inception of the dissociation effect in atoms comprising the boundaries of slip units. These are of insufficient volume to affect the electrical conductivity or line broadness to any extent, but the rate of etching is apparently dependent on the condition at the boundaries, since observations with sensitive reagents show initial attack occurs at such points. This boundary distortion is apparently the major factor in the hardening of iron on cold work and in microscopic recrystallization. This is substantiated by the fact that the last stage in the process coincides with the softening period. As outlined under steps 4 and 5 in the discussion on copper, the softening and gross recrystallization stages are conceived as the complete elimination of boundary distortion and movements of the reorganized atom blocks into suitable orientations for reunion into microscopic grains.

Recovery of Nickel—The recovery of nickel is of interest, since this element crystallizes in the same lattice system as copper, while it is comparable to iron in that it is a neighboring ferro-magnetic

element. Accordingly, it would be expected that the curves for nickel should resemble in some respects both the previously named elements. The curves of Fig. 22 confirm this assumption. The electrical conductivity is recovered at much lower temperatures than are the hardness and magnetic induction effects. In fact, a slight hardening ef-

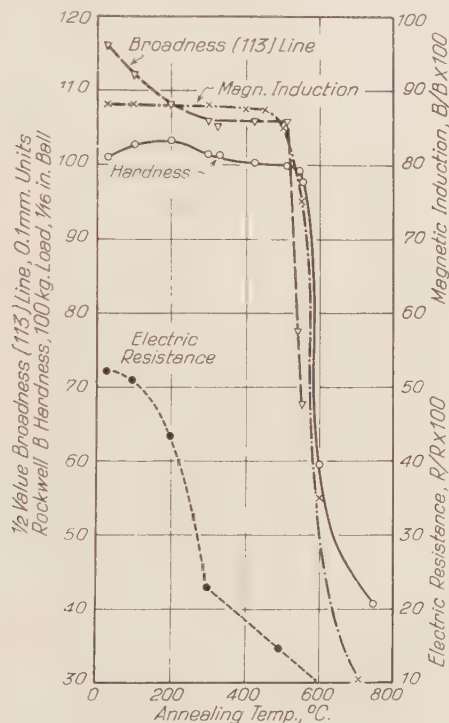


Fig. 22—Recovery of Cold-Worked Nickel.

fect is noted in the temperature range of maximum recovery rate for the conductivity. A slight drop in line broadness is noted in the temperature range 100 to 300 degrees Cent. (210-570 degrees Fahr.), which corresponds to the first stage of electrical recovery.

The difference in temperatures for the main drops in hardness and line broadness is not large but the broadness falls off at definitely lower temperatures than the hardness. For instance, the hardness after a 1-hour anneal at 548 degrees Cent. (1020 degrees Fahr.) is unchanged, while the broadness as measured on the same specimen has decreased from 10.6 to 7.6 on the arbitrary scale of half-value measurements.

It is worthy of note that the magnetic recovery takes place in the same temperature range as the hardness recovery. This fact may be taken to indicate that the magnetic induction phenomena are intimately connected with boundary conditions.

Time-Temperature Law of Recovery of Nickel—In Fig. 8 the temperatures at which nickel was annealed to attain a constant line sharpness has been plotted in arithmetical coordinates against the corresponding time in minutes as logarithmic abscissae. Thus plotted, the points follow a straight line within the experimental error. Van Liempt (18) assumes that recrystallization consists of a place change of the fraction of atoms in the distorted metal lattice whose energy corresponds to a certain minimum vibration amplitude, and that the

"Springzeit" (jumping time) of a diffusing atom is $B = \frac{1}{4\nu}$, where ν is the characteristic vibration frequency according to Einstein's specific heat theory. By analogy with kinetic gas theory, he then shows that the time of place change in all directions for the majority of lattice points is

$$t = \frac{1}{6} \cdot \frac{3}{2\nu} \cdot e^{\frac{3b^2T_s}{T_R}} \cdot \frac{K\beta}{T_R}$$

where K and b are constants, T_R and T_s are, respectively, recrystallization and melting temperatures in absolute Centigrade units and β is a measure of the degree of deformation. From this, for a given specimen of cold-worked metal,

$$T_R = \frac{\text{constant}}{\log_{10} t - \log_{10} \frac{1}{4\nu}}.$$

For the case of recovery from line broadness, van Liempt's assumption that the vibration time for place change is equal to one-fourth the period of the atom may be modified, since the atoms are displaced from their normal positions by rather small amounts in relation to the interatomic distance. However, the data of Table VI show constant values within 1.5 per cent of the mean if the values for the $\frac{1}{2}$ - and 1-hour anneals are omitted. Since it was noted that the latter recovery curves tended to flatten with increased annealing temperatures, it is entirely possible that the extrapolations are in error for the short-time anneals.

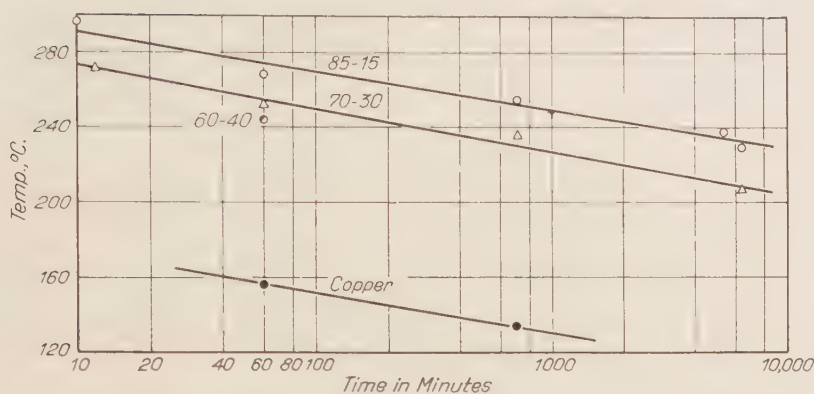


Fig. 23—Time and Temperature of Annealing for Recovery of Constant Line Sharpness in Copper and Copper-Zinc Alloys.

The series of annealing experiments conducted at 512 degrees Cent. (955 degrees Fahr.) show (Fig. 9) that contrary to the findings of Burgers and van Arkel (8) on tungsten, the line sharpening

Table VI*

t (sec.)	T _R (Deg. C. abs.)	T _R (log ₁₀ t + 13.50)
1,800	855	14,300
3,600	845	14,500
18,000	838	14,900
93,600	822	15,300
151,200	805	15,000
345,600	799	15,200

*The value for $-\log_{10} \frac{1}{4\nu}$ is derived from Lindemann's equation, which yields, $\nu N_1 = 8.1 \times 10^{12}$.

of nickel at low annealing temperatures consists not only of the rapid initial drop noted by these authors, but also a long induction period followed by a gradual sharpening corresponding to a diffusion process. This indicates that at the chosen annealing temperature the fraction of atoms whose energy content is sufficient for diffusion

$$= K_1 e^{\frac{K_2 \beta}{T_R} - \frac{b^2 T_s}{T_R}}$$

is small for heating times less than 26 hours.

ALLOY SYSTEMS

Copper-Zinc—The effect of annealing time on temperature of line sharpening was studied in the 85-15 and the 70-30 brass. The results are plotted as for pure nickel in Fig. 23, together with the data

obtained on 60-40 brass and copper. The experimentally derived constants for these curves corresponding to those of the equation for nickel are summarized in Table VII.

Table VII

Material	Constant	$-\log_{10} \frac{1}{4n\tau}$
Copper	6,800	15.7
85-15 brass	13,100	14.5
70-30 brass	10,061	15.3

The fact that the vibration constant is somewhat larger than predicted by use of van Liempt's assumption is in accord with the nature of the recovery from line broadness. In this process it is thought that recovery consists of return to normal positions rather than a place change as conceived by van Liempt.

Relation of Line Broadness to Season Cracking in 70-30 Brass—

It is well known that copper-zinc alloys in the cold-worked state are subject to failure by the formation of spontaneous cracks. There has been much speculation concerning the cause of this type of failure. Many investigators have shown that annealing at temperatures under the softening point is sufficient to remove the cause of such failures. It has been the general consensus of opinion among metallurgists that internal stresses of some sort were the cause of the season cracking phenomena, but the exact nature of these stresses has never been satisfactorily explained.

Moore and Beckinsale (20) in 1920 made a thorough investigation of the times at various annealing temperatures necessary to prevent accelerated cracking in mercurous nitrate solution. Their results showed that the temperature for the attainment of this immunity to mercury salts was definitely decreased as the annealing time is increased. They did not, however, attempt to formulate a quantitative time-temperature relationship due perhaps to the experimental spread in their results. However, if their data are plotted with the time in logarithmic and the temperature in arithmetical units, and a line drawn through the points thus obtained, the solid curve of Fig. 24 results. The broken line curve is a reproduction of the line sharpening curve for 70-30 brass in Fig. 23 plotted to the same scale as the mercury tests. It is also interesting to note the close agreement obtained on the 1-hour test of W. B. Price (21) to the 1-hour line sharpening temperature of the present investigations. While the slopes of the two lines do not agree particularly, the temperature

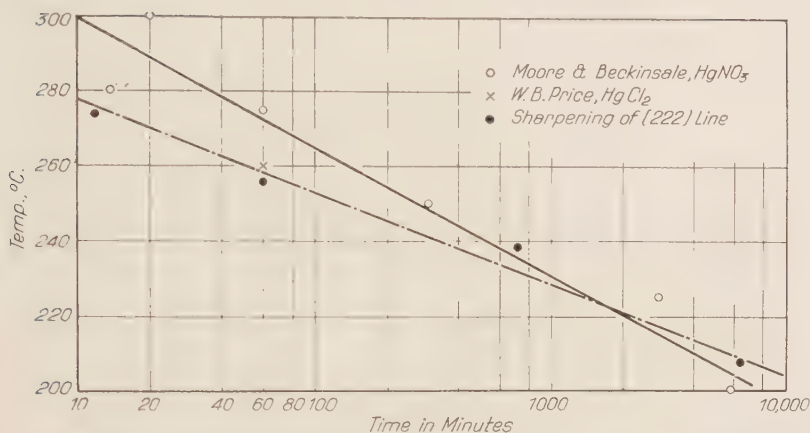


Fig. 24—Removal of Internal Stress in 70-30 Brass as Shown by Sharpening of Hull-Debye Lines and by Accelerated Cracking Tests in Solutions of Mercury Salts.

range and trend is the same for both sets of data. A much better agreement in slope would have been obtained had the 20-minute and 100-hour points been omitted from Moore and Beckinsale's data.

The close agreement of the line broadness data with the results of Moore and Beckinsale indicates that the internal stresses which cause season cracking are somehow associated with the line broadening. This in itself does not clarify the mechanism by which brass fails spontaneously on aging after cold work, but the phenomenology of season cracking can be satisfactorily explained in terms of the hypothesis of the present thesis with the knowledge of these facts.

In the periodic bending or crumpling of the lattice segments which give rise to the broadening of X-ray lines, the distances between various atom pairs, or even in the whole set comprising the block, are changed. This strain, of course, in mechanical terminology is accompanied by an equivalent stress, provided it is elastic in nature. Calculations by Caglioti and Sachs (10) have shown that only a few per cent of the energy stored in the lattice can be ascribed to elastic stress. However, this distortion may also affect the atoms in such a way that the bondings of molecular type are increased, thus storing added energy in unstable molecular configurations. The energy content of the various atoms in a block is distributed in a statistical manner, with the most highly distorted atoms probably in the boundary layers. Investigation¹ of electrical conductivities has shown that

¹Tammann and Dreyer, *Ann. der Phys.*, Vol. 16, 1933, p. 657, noted a 2-stage recovery of electrical conductivity in copper-zinc alloys with inflection points at 80 and 220 degrees Cent. (430 degrees Fahr.) for the 28 per cent zinc alloy.

changes in the degree of binding of the valence electrons begin to take place at relatively low temperatures. This is particularly evident in the copper-zinc alloys which show a recovery effect which may apparently be ascribed to the zinc atom at temperatures in the neighborhood of 100 degrees Cent. for 1-hour anneals. In view of the results obtained by Goetz and Focke (22) on bismuth alloys, this may indicate that the zinc atoms are concentrated on certain atomic planes designated as π planes. If such a structure were assumed for brass, such planes would be the most favorable for slip; thus, the boundary planes of slip lamellae are probably higher in zinc than the body of the slip lamellae.

On heating, the energy distribution of a block tends naturally toward a level. However, due to the restrictions imposed by the boundaries, the readjustments evidenced by freeing of valence electrons (increased electrical conductivity) lead to an actual increase in energy at the boundary planes.

The assumption of this state is a corollary to the fact that the change of line broadness is very small, indicating that the total amount of distortion is practically unchanged. This increase in energy of the boundary atoms is used as an increase in the molecular bondings of these atoms, thus building up local stress concentrations at grain boundaries which exceed the tensile strength of the alloy.

On annealing at higher temperatures, the second stage in recovery, made possible by the loosening of interatomic bindings, occurs. This is the actual diffusion of displaced atoms to normal position as evidenced by the sharpening of lines. When this sharpening reaches a certain stage, the boundary atom deformations begin to disappear. *It is the inception of the latter state of the recovery process which is of importance in the elimination of "season cracking" tendencies in brass.* As was previously shown, the temperature difference between the boundary atom recovery and the general lattice recovery is small for this metal. This indicates the reason for the similarity of temperature for the definite decrease in chemical reactivity of the boundary atoms as shown by the mercury salt tests, and the recovery from lattice distortion as shown by the line broadness data.

Relation to Creep Properties

In the preceding discussion it was pointed out that the line sharpness recovery temperature of the brasses possessed a maximum

at an intermediate composition in the alpha range. This is brought out more clearly in Fig. 25, which shows the results for the 1-hour anneals on copper and the brasses plotted in relation to the zinc content. It is seen that for the alloys studied the recovery temperature is at a maximum for 15 per cent zinc. This is in agreement, not only with the electrical conductivity results of Tammann and Dreyer, who

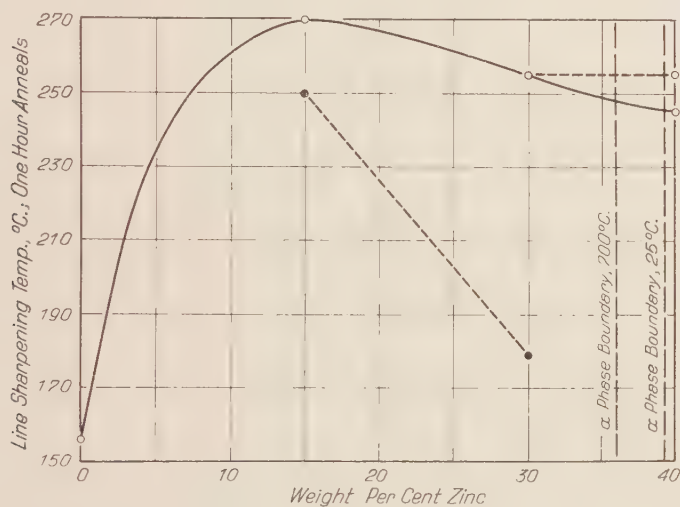


Fig. 25—Copper-Zinc Alloys. Relationship of Zinc Content. Line Sharpening and Creep.

found the recovery range highest in the 10 per cent zinc alloy, but also with some experiments on hot hardness performed by Meneghini (23) and by Doerinckle and Trocke (24). The former found that the alloy containing 20 per cent zinc required the highest temperature for penetration of a steel cone under constant pressure, the latter that for 50 per cent compression, minimum compressibility occurred at approximately 15 per cent zinc. These results are also confirmed by the work of Clark and White (25) on the creep characteristics of the alloys used in this investigation. Their data for creep at 315 degrees Cent. (600 degrees Fahr.) are also reproduced in Fig. 25 for the 85-15 and the 70-30 compositions. The results for the 60-40 composition were not obtained at this temperature, but from the low value obtained at 205 degrees Cent. (400 degrees Fahr.), it is believed that the stress for creep of the same magnitude would be only a few pounds.

The results obtained by Clark and White would not have been

so marked in their difference in stress values for the 0.01 per cent strain per 1000 hours at 315 degrees Cent. (600 degrees Fahr.), had the 85-15 and the 70-30 materials been in similar initial condition. The 70-30 material had been cold drawn previous to testing. Clark and White² have found in the case of a carbon steel that stretching at room temperature previous to the creep test has the effect of marked reduction of the limiting creep stresses at temperature from 800 to 1000 degrees Fahr. (425 to 540 degrees Cent.). The cold-drawing increases the tendency toward recovery at the test temperature, and thus upsets the equilibrium between the rates of isothermal strain hardening and recovery which normally obtains in the creep test. However, the difference in creep stress between the 85-15 and 70-30 would seem to be too large to be ascribed entirely to this cause, particularly in view of the evidence on hot-hardness and X-ray line sharpening. It may accordingly be concluded that there is some factor in the addition of zinc to copper which causes the maximum stability at high temperatures to occur at a composition somewhere in the neighborhood of 15 per cent zinc.

Copper-Nickel Alloys—The relation of temperature of line sharpening at constant annealing time to the relative creep properties of a series of alloys is substantiated by the relation between these factors for the Adnic and Monel metal compositions. The creep properties at various temperatures for these alloys have been obtained by Clark and White.³ They are summarized, together with the line sharpening temperature of the respective alloys, in Table VIII.

Table VIII
Creep Properties

Stress for Creep of 0.01 Per Cent per 1000 Hrs. at T. Deg. C.		Inflection Points of Line Sharpening Curves	
T Deg. C.	Pounds per Square Inch	T Deg. C.	
Monel 315	26,000		
427	19,000	590	
538	1,600		
Adnic 315	13,800		
427	4,500	450	
538	630	570	

It is apparent that both the high temperature stability and the line sharpening temperatures are a maximum for the Monel metal composition, which incidentally confirms the findings on the brasses that the maximum temperature stability is found near the middle of the continuous series of solid solutions in terms of atomic percent-

²Private communication.

³Clark and White, *Transactions*, American Society of Mechanical Engineers, Vol. 53, 1931, FSP-53-15, p. 183-191.

ages. It is believed that while the actual values for creep stresses may be affected by the impurities other than copper and nickel in these alloys, the trend of the values is controlled by the main components, particularly in solid solution alloys of this type.

Pearlitic Aligned Steels of Varying Manganese Content—It was shown in the experimental part that the series of steels ranging from one to three per cent manganese exhibited a unique phenomenon on annealing the cold-worked specimens in the temperature range 400-500 degrees Cent. (750-930 degrees Fahr.). The alloys in general showed an initial recovery from line broadening which was, however, interrupted by a line-broadening lattice distortion from another cause on annealing at slightly higher temperatures. This secondary lattice distortion was accompanied or paralleled by an increase in Rockwell hardness which indicates that the noted X-ray phenomena are probably due to a precipitation hardening effect.

Before proceeding to a discussion of the possible causes and implications of the observed precipitation effect, the effect of the addition of molybdenum and vanadium to the ternary iron-manganese carbon alloy may be reviewed. In Fig. 26 are reproduced the X-ray recovery curves for steels MM6, MM2 and QV, all containing approximately 2 per cent manganese. MM2 and QV contain in addition 0.21 and 0.32 per cent molybdenum, respectively, and QV also has a vanadium content of 0.20 per cent. In comparing these curves, it is apparent that 1, the additional alloys have the effect of: Reducing the slope of the initial recovery from line broadening. 2, of Displacing the secondary broadening phenomena to higher temperature regions.

The effect "1" is quantitatively expressed in Table IX, which indicates the slopes $\Delta B/\Delta T$ where B is line broadness and T is tem-

Table IX

	Effect of Alloys on $\frac{\Delta B}{\Delta T}$				
	B_1	B_2	T_1	T_2	$\Delta B/\Delta T$
Steel					
MM6	11.6	6.9	400	425	0.188
MM2	12.7	8.3	400	450	0.0881
QV	11.5	6.9	350	475	0.0368

perature. Since the molybdenum content is increased 50 per cent in addition to the vanadium content, it is impossible to evaluate the effect of vanadium in decreasing the slope of the QV alloy.

In the analysis of this decrease in slope, however, the effect of the secondary broadening phenomenon should be particularly considered. The temperature range of the initial recovery from line broadness is conditioned by two factors in these alloys. First, the inherent characteristics of the recovery from cold-working, which

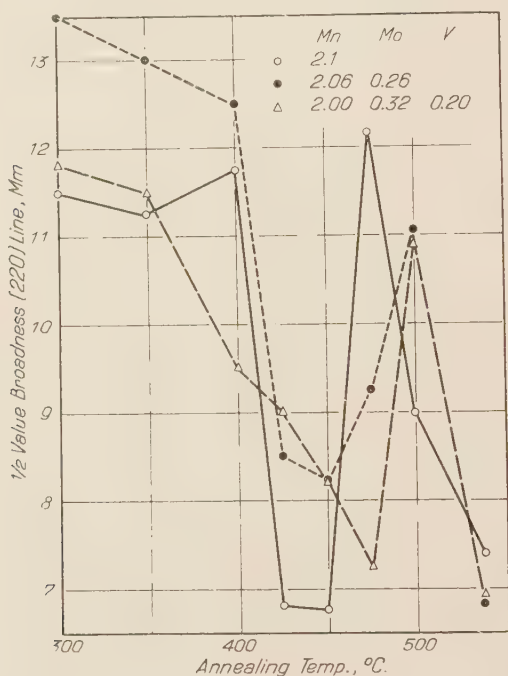


Fig. 26—X-Ray Recovery Curves for Steels. One-Half Value Broadness (220) Line MM.

has been shown to differ widely in the pure metals; and second, the temperature at which the precipitation effect becomes noticeable in the line broadening. These overlapping effects are shown in the hypothetical curves reproduced in Fig. 27.

In Fig. 27, Curve 1 represents the normal recovery trend of the solid solution alloy. Curve 2 the line-broadening at various annealing temperatures due to precipitation effects, and Curve 3 is the summation curve of 1 and 2. Curve 3 is the experimentally observed effect. From this picture it is seen that the position of the minimum point "a" is dependent on the temperature of the maximum point "b" and upon the slope of the curves 1 and 2 near the point of intersection. These variations are apparent in the changed appearance of the man-

ganese-molybdenum series as the manganese content is increased. In the 1.1 per cent manganese alloy, practically no precipitation effect is present, and a normal curve of recovery from line-broadening caused by cold work results. The 1.25 per cent manganese steel indicates that the secondary broadening is approaching its maximum before

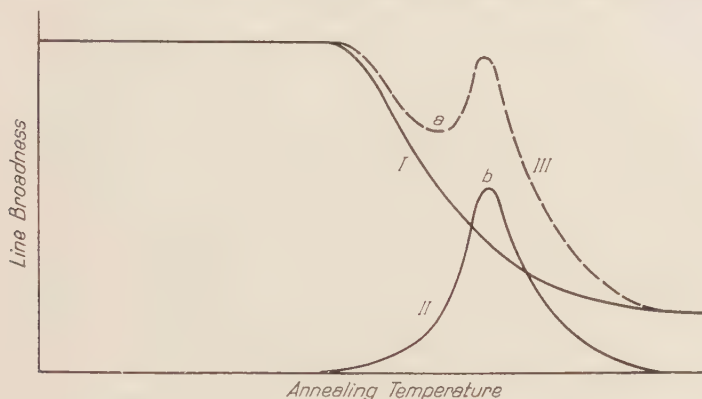


Fig. 27—Overlapping Effects as Shown by Hypothetical Curves.

recovery from line broadness due to cold work has reached a rapid rate. This means that either Curve 1 is displaced toward higher temperatures, or that Curve 2 is displaced toward lower temperatures, or both. In the light of other experimental evidence such as the small magnitude of the hardness change and the temperature at which it occurs, one is inclined to the former hypothesis. In the next alloy of the series a distinct separation of the two effects is first evident. The MM9 alloy containing 1.75 per cent manganese shows a distinct tendency for the precipitation effect to be displaced toward higher temperature regions. This temperature effect is not proportional to manganese content, since the temperature of the maximum drops to 450 degrees Cent. (840 degrees Fahr.) in the 2.0 per cent manganese steel; although, as the hardness measurements show, the magnitude of the precipitation effect increases with the manganese content. For instance, in the MM8 (1.25 per cent manganese) steel the precipitation hardening amounts to only a 0.7 point Rockwell "B" increase, while the MM2 (2.06 per cent manganese) has a total increase of 3.5 points Rockwell "B."

These considerations lead to two possible explanations of the precipitation effect:

1. The iron-manganese solid solution, due to heterogeneities, is precipitating the epsilon phase, or
2. Precipitation of complex carbides of manganese occurs on annealing the cold-worked alloys.

In support of the first hypothesis, the recent publication of Walters (26) and co-workers on the binary iron-manganese alloys indicates that marked heterogeneity of composition within the individual crystals may occur in slowly cooled alloys and that the tendency toward the formation of epsilon is increased by cold-working. This would make the precipitation of epsilon particularly favorable under the present experimental conditions.

In support of the second hypothesis, the work of W. A. Wood (27) on broadening of lines on annealing tungsten magnet steels caused him to conclude that the broadening in those steels was due to carbide precipitation. Cold work is known also to cause an increased tendency toward carbide precipitation, and the effect of molybdenum and vanadium in displacing the secondary broadening effect toward higher temperature ranges might be taken as an indication that the carbides are the precipitated phase, inasmuch as these alloying elements are known to be remarkable carbide stabilizers. This evidence is not conclusive, however, since the unknown effect of molybdenum and vanadium on the stability of the iron-manganese solid solution is also involved.

A third possibility, that the observed effect is due to a combination of the hypotheses offered above, seems entirely reasonable; the latter hypothesis is perhaps the best compromise obtainable in the lack of entirely conclusive evidence.

These alloys have been subjected to extensive high temperature creep studies by A. E. White and C. L. Clark, of this laboratory. In view of the correlation obtained of creep results with the X-ray studies, in the case of the copper-zinc alloys, it is more or less to be expected that some light may be thrown on the relative creep properties of the manganese steels by the results of the present investigation. The creep test data on the steels of the MM series obtained at 900 degrees Fahr. (480 degrees Cent.) are summarized in Table X.

These data are graphically presented in Fig. 28, along with the X-ray line broadness results. It will be noted that the first maximum in the creep stress curve at 900 degrees Fahr. (480 degrees Cent.) occurs at the same composition as the maximum temperature of initial sharpening, the second maximum coincides with composition of

Table X
Stresses for Creep of 0.01 Per Cent per 1000 Hours at 900 Degrees Fahr.
(480 Degrees Cent.) in Selected Manganese-Molybdenum Steels

Designation	Per Cent Manganese	Stresses Pounds per Square Inch
MM10	1.10	10,200
MM8	1.25	21,000
MM1	1.46	10,200
MM9	1.75	16,000
MM2	2.06	9,600
MM4	2.99	7,000

alloy which has the highest temperature of the inception of line broadening effect.

This indicates that the creep properties of the manganese-molybdenum steels are due partially to the properties of the normal solid solution and pearlite mixture and partially to the precipitation effect. If the precipitation is excluded from consideration, the 1.25

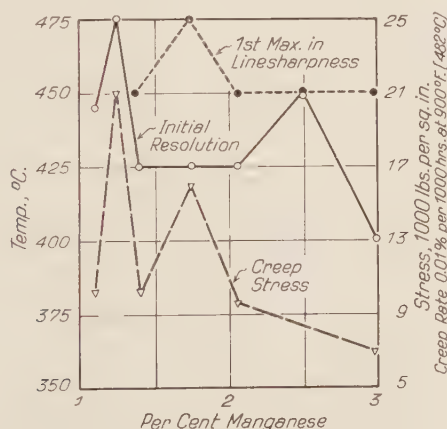


Fig. 28—Line-Sharpener Temperatures and Creep Stress at 90 Degrees Fahr. of Manganese-Molybdenum Steels on Annealing as a Function of the Manganese Content.

per cent manganese composition seems to be the alloy of critical composition from the standpoint of temperature stability of strength; this alloy may be compared to the 85-15 brass of the copper-zinc system. In the same way that the greater temperature stability of that alloy was shown by its slightly higher recovery temperature from X-ray line broadening, so the 1.25 per cent manganese steel shows that its solid solution is of the optimum composition by the extension of its recovery range to such high temperatures that the precipitation effect sets in before any sharpening is observed.

The 1.75 per cent manganese steel exhibits the effect of a critical concentration of precipitating substances for attainment of long time strength at 900 degrees Fahr. (480 degrees Cent.).

The high temperature properties of the QV steel are of interest since this steel has almost identical creep properties at 900 degrees Fahr. (480 degrees Cent.) to the MM8 composition. The logarithmic

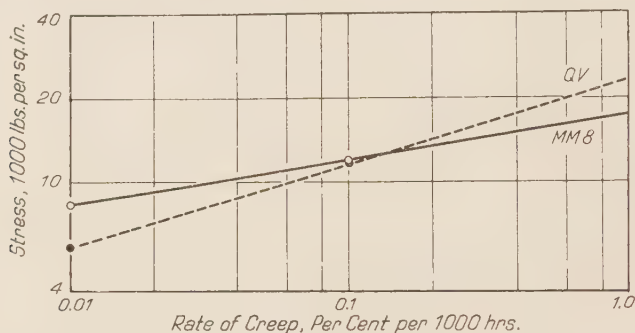


Fig. 29—Creep-Stress Curves for MM8 and QV Steel at 1000 Degrees Fahr.

creep stress curves for these two compositions are reproduced in Fig. 29. It is apparent that the MM8 is somewhat superior at 1000 degrees Fahr. (540 Cent.) for the low rate of creep (0.01 per cent per 1000 hours) but that the QV has a greater slope and becomes equal in strength to MM8 at a creep rate of 0.1 per cent per 1000 hours.

The line broadness recovery curve of the QV steel indicated initial recovery at a much lower temperature than the MM8 but showed a very broad temperature range of recovery, and a precipitation effect displaced toward higher temperatures than most of the steels investigated. A low rate of line sharpening may thus indicate a greater tendency toward strain hardening at elevated temperatures.

SUMMARY

1. The broadness of Hull-Debye-Scherrer lines of selected cold-worked metals and alloys has been investigated as a function of temperature and time of annealing. The effect of deformation temperature on the broadness of lines of aluminum and copper was also investigated. The recovery from line broadness on annealing can be treated as a diffusion process. At low annealing temperatures the recovery is characterized by a long induction period followed by a

gradual increase of line sharpness. Results on nickel, copper and 85-15 and 70-30 brass indicate the following relation between time and temperature of annealing for attainment of constant line sharpness:

$$T_R = \frac{\text{constant}}{\log_{10} t - \log_{10} \frac{1}{4n\nu}}$$

2. The results have been correlated with electrical conductivity, magnetic susceptibility and hardness data. It is shown that the lattice distortion responsible for most line broadening is of a different nature than that involved in the hardness and electrical changes. The electrical conductivity changes on cold-working are due to interatomic binding of "free" electrons in the body of the lattice due to distortion of electron shells, while hardness and magnetic changes are due to similar forces acting on grain and slip lamella boundary atoms, according to the writers' hypothesis.

3. It was shown that line sharpening of 70-30 brass closely parallels existing data on relief anneals for elimination of season cracking tendencies. The hypothesis is advanced that season cracking is due to redistribution of interatomic forces leading to abnormal cohesion forces at grain boundaries.

4. Correlation with existing creep data shows that maximum creep properties coincide with maximum line sharpening temperatures. Similar parallelism is indicated by experiments on Admic and Monel metal. The poor temperature stability of 60-40 brass is shown to be due to the fact that the recovery temperature of the beta phase is distinctly lower than that of the alpha. The use of the X-ray method is thus shown to be applicable to the analysis of recrystallization phenomena in complex alloys in which the microscopic evidence is confusing.

5. Recovery of a series of cold-worked pearlitic steels of varying manganese content from line broadness was investigated. It was found that there is superposed on the normal recovery curve a re-broadening due to a precipitation hardening effect. Correlation with creep data of White and Clark shows that first composition of optimum strength at 900 degrees Fahr. (480 degrees Cent.) (1.25 per cent manganese) coincides with maximum temperature of line sharpening, and that a second composition (1.75 per cent manganese) which also has exceptional creep characteristics corresponds to maximum temperature for inception of precipitation effect.

6. Effect of additions of molybdenum and vanadium to the manganese steels is to reduce rate of line sharpening with respect to temperature, indicating that diffusion of atoms of cold-worked iron-manganese solid solution is inhibited by these alloys.

7. The correlations with creep data indicate that the line sharpening temperatures of a given series of alloys may be an indication of their relative creep characteristics.

ACKNOWLEDGMENTS

The authors are indebted to the following individuals and firms for the donation of metal samples—Dr. J. T. Eash of the International Nickel Co., for the Grade A, carbon-free nickel; D. L. Summey, of the United States Metals Refining Co., for the OFHC copper; and to Dr. C. L. Clark, of the Department of Engineering Research of the University of Michigan, for the brasses, Admic, and Monel metal, and the series of manganese and manganese-molybdenum steels.

They are especially grateful to Prof. A. E. White and Dr. C. L. Clark for permission to use certain unpublished creep data, and to the latter for many helpful discussions.

The Departments of Chemical Engineering and Engineering Research of the University of Michigan very generously provided Mr. Wilson with research assistantships, under the terms of which the experimental work was carried out.

References

1. A. E. van Arkel, *Physica*, Vol. 5, 1925, p. 208-212.
2. W. P. Davey, *General Electric Review*, Vol. 28, 1925, p. 588.
3. U. Dehlinger, *Zeitschrift für Kristallographie*, Vol. 65, 1927, p. 615-631.
4. W. A. Wood, *Proceedings*, Physical Society of London, Vol. 44, 1932, p. 67-75.
5. K. Becker, *Zeitschrift für Physik*, Vol. 42, 1927, p. 226.
6. U. Dehlinger, *Annalen der Physik*, 2, Vol. 5, 1929, p. 749-793.
7. S. Sekito, *Science Reports*, Tohoku Imperial University, Vol. 16, 1927, p. 343-355.
8. W. G. Burgers and A. E. van Arkel, *Zeitschrift für Physik*, Vol. 48, 1928, p. 690.
9. W. A. Wood, *Nature*, Vol. 131, 1933, p. 842.
10. V. Caglioti and G. Sachs, *Zeitschrift für Physik*, Vol. 74, 1932, p. 647.
11. F. Sauerwald and W. Globig, *Zeitschrift für Metallkunde*, Vol. 25, 1933, p. 33.
12. W. Koster, *Zeitschrift für Metallkunde*, Vol. 20, 1928, p. 189.
13. G. Tammann and K. L. Dreyer, *Annalen der Physik*, Vol. 16, 1933, p. 111-119.

14. R. S. Dean and J. L. Gregg, "General Theory of Metallic Hardening," *Proceedings*, Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, 1927, p. 368-394.
15. Zay Jeffries and R. S. Archer, "Science of Metals," McGraw-Hill Book Company, New York City, 1924.
16. Messrs. Hengstenberg and Mark, *Zeitschrift für Physik*, Vol. 61, 1930, p. 435-453.
17. Lyall Zickrick and R. S. Dean, "Note on the Distribution of Energy in Worked Metals and the Effect of Process Annealing Temperature on the Final Annealing Temperature of Fine Copper Wire," *Proceedings*, Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, 1927, p. 368-394.
18. J. A. M. van Liempt, *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 195, 1931, p. 366-386.
19. G. Tammann and Moritz, *Annalen der Physik*, Vol. 16, 1933, p. 567.
20. H. Moore and S. Beckinsale, *Journal*, Institute of Metals, Vol. 23, 1920, p. 225-244.
21. W. B. Price, *Proceedings*, American Society for Testing Materials, Vol. 18, Part 2, 1918, p. 179.
22. A. Goetz and A. B. Focke, *Physical Review*, Vol. 45, 1934, p. 170-199.
23. D. Menneghini, *Industria*, (Milan) Vol. 34, 1920, p. 71-74. Also, *Journal*, Institute of Metals, Vol. 24, p. 445-446.
24. Mr. Doerinckle and J. Trocke, *Zeitschrift für Metallkunde*, Vol. 13, 1921, p. 305-312.
25. C. L. Clark and A. E. White, "Influence of Recrystallization Temperature and Grain-Size on the Creep Characteristics," *Proceedings*, American Society for Testing Materials, Vol. 32, No. 2, p. 492.
26. F. M. Walters, Jr., "Alloys of Iron and Manganese, Part IX," *TRANSACTIONS*, American Society for Steel Treating, Vol. 21, p. 1002.
27. W. A. Wood, *Philosophical Magazine*, Vol. 13, 1932, p. 355-360.

